External occupational exposures in some NORM industries located at the South-West of Spain

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Abstract. Detailed mappings of the external exposures which can be received by the workers in two NORM industrial factories located at the South-West of Spain have been performed: one devoted to the production of phosphoric acid, and the other devoted to the production of titanium dioxide pigments. In most places of the analyzed factories, the external exposures are moderated, although in some specific points, and associated to the presence of scales, their values are clearly higher. Nevertheless, under normal running conditions, the contribution of the external exposures to the effective doses received by the workers is lower than 1 mSv/y because the worker occupancy factors values are very low in the places with the highest external exposures.

Keywords: NORM, external exposures, scales, phosphoric acid, titanium dioxide
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INTRODUCTION

During the last twenty years has grown sharply the awareness in the scientific community about the necessity to evaluate the radiological impact associated to industrial activities which either use in their production process raw materials enriched in natural radionuclides or are producing by-products or residues enriched in these radionuclides (NORM industries).

On this frame, we are analysing the occupational and environmental radiological impact caused by several chemical industries located in the South-West of Spain.

In this work, we expose the main conclusions obtained from the mapping of the external exposures susceptible to be received by the workers in two NORM industrial activities: one devoted to the production of P_2O_5 by treating sedimentary phosphate rock, and the other devoted to the production of TiO_2 pigments through the treatment of a heavy mineral called illmenite. For a better understanding of the obtained results, a brief description of both production processes, and a simplified explanation of the radionuclide fluxes along the processes will be given.

EXPERIMENTAL

External exposures were determined in the analysed factories by using a calibrated Berthold LB1230 monitor with the environmental probe LB123. All the measurements were corrected by subtracting the background value determined in an area located in the surroundings. Consequently, all the values shown in this work will give the additional external exposures which can be received by the workers during their activities inside the factories.

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DESCRIPTION OF THE INDUSTRIAL PROCESSES

In Figure 1 is described schematically the process of P_2O_5 production applied in the analysed factory. This production process have the following four main steps: a) milling of Moroccan phosphate rock until approaching a grain-size compatible with an effective acid attack, b) attack of the milled rock with concentrated sulphuric acid. (In this digestion step is formed a "cake" containing in dissolution the P_2O_5 and a solid fraction called phosphogypsum), c) separation of the phosphoric acid though filtration of the "cake" formed in the digestion, and d) concentration of the phosphoric acid by evaporation until the desired level.

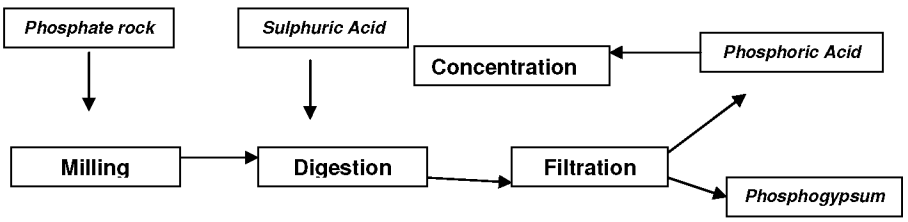

FIGURE 1. Scheme of the production process in the Phosphoric Acid Plant

The Moroccian sedimentary rock treated in the factory is clearly enriched in radionuclides from the uranium-series (^{238}U concentrations ranging from 1000 to 1500 Bq/kg), with all the daughters in secular equilibrium, while the concentrations of the thorium series radionuclides are clearly lower and similar to the found ones in Spanish unperturbed soils. During the production process, a clear radioactive fractionation occurs, with more than 90% of the ^{226}Ra and around 70% of ^{230}Th being accumulated in the phosphogypsum, while, on the contrary, the majority of U is associated with the P_2O_5. The typical concentrations of ^{226}Ra in the dried phosphogypsum ranges between 600 and 900 Bq/Kg, while the concentrations of the U-isotopes in the P_2O_5, before concentration, ranges between 900 and 1200 Bq/kg.

In Figure 2 is described schematically the process of titanium dioxide pigment production applied in the analysed factory. For the production of the mentioned pigment, a heavy mineral enriched in Ti and Fe (illmenite) is treated. This production process is divided in the following steps: a) milling of the illmenite, b) digestion of the milled rock with concentrated H_2SO_4, reduction of the resulting cake and separation (clarification) of the inattacked residue from the dissolved fraction, d) precipitation of the TiO_2 by hydrolysis, from the dissolved fraction, , e) separation of the titanium dioxide pulp by filtration, f) washing of the pulp, g) calcination of the pulp, and h) conditioning of the titanium dioxide by milling, coating, drying and grounding until obtaining the desired final commercial pigment.

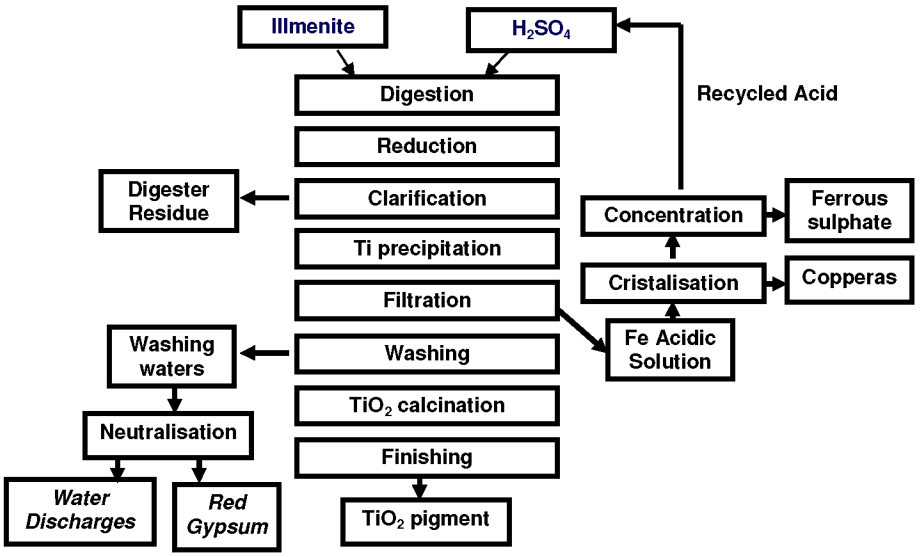

FIGURE 2. Scheme of the production process in the Titaniu Dioxide Plant

In the separation of the TiO_2 pulp by filtration is generated a strong acid solution, rich in metallic sulphates, which is treated to obtain sequentially, and as co-products, ferrous sulphate heptahydrate (copperas) by crystallization, and ferrous sulphate monohydrate by concentration.

In the washing and purification of the separated TiO_2 pulp is also generated a slightly acidic water solution. The acidity of this solution and its heavy metal content is removed before its discharge in the Huelva estuary through its neutralization with calcium hydroxide. In this neutralization, a co-product called red gypsum is formed.

The illmenite rock contains radionuclides from the uranium (^{238}U: 100 to 150 Bq/kg) and thorium series (^{232}Th: 300 to 400 Bq/kg) with all the daughters in secular equilibrium. During the production process, a clear radioactive fractionation occurs, with the majority of the Ra isotopes being associated to the digester residues (^{226}Ra: 600-800 Bq/kg, ^{228}Ra: 1800-2200 Bq/Kg).On the contrary, the majority of U and Th is associated to the dissolved liquor formed in the digestion and flow along the process until they finish associated mainly with the ferrous sulphate monohydrate co-product (The U and Th remain mainly in the acidic solution when the TiO_2 is precipitated). The commercial pigment and the co-product copperas are free of radionuclides, while the presence of U and Ra in the red gypsum is moderate (lower than 100 Bq/Kg).

EXTERNAL OCCUPATIONAL EXPOSURES

In Table 1 are compiled the instantaneous external exposures (mSv/h), over background, determined along the phosphoric acid production process. The indicated values are reflecting then, the net contribution related with the industrial activity.

TABLE 1. External exposures (mSv/h) over background determined along the phosphoric acid production process. The number of determinations performed in each process step is also indicated.

Process Step	Instantaneous dose rates over background (μSv/h)	Process step	Instantaneous dose rates over background (μSv/h)
Milling, n= 10	0.03 -0.37	Filtration 1, n= 3	0.17 – 1.05
Reaction, n = 4	0 – 0.10	Filtration 2, n=3	0.17 – 0.98
Concentration, n=2	0.05 – 0.45	Filtration 3, n=5	0.10 – 1.36
Recycling, n=5	0.04 -0.50	Decantation, n=5	0.04 – 0.50

The higher effective doses rates have been obtained inside the filtration zone, where dry gypsum is managed. However, in the filtration zone the occupation factor by the workers is low. As a consequence, under normal running conditions, the contribution in all the places of the external exposures to the effective doses received by the workers is lower than 0.5 mSv/year.

Some spots with higher radionuclide concentrations have been found along the process. They correspond with sludges formed in the tanks where the P_2O_5 is decanted and with scales formed in the filtration step. Its effect in the measured external exposures is nevertheless limited due to the shielding done by the walls of the tanks and/or by the filtration system. Special precautions should be taken from the radiological point of view when these spots are removed during maintenance operations in the plant.

In Table 2 are compiled the instantaneous external exposures (mSv/h) over background determined along the titanium dioxide pigment production process. In most places the instantaneous external dose rates are moderate, with only higher values in the store where the digester residues are accumulated before its management (doses correlated with the high Ra-isotopes concentrations present in this residue) and, specially in the crystallisation and filtration areas. In these last areas the higher doses are associated to the presence of “scales”, heavily enriched in Ra-isotopes, attached to tubes (crystallisation) or filters (filtration).

TABLE 2. External exposures (μSv/h) over background determined along the titanium dioxide production process. 150 mesurements were performed

Process Step or store	Instantaneous dose rates over background (μSv/h)	Process step or store	Instantaneous dose rates over background (μSv/h)
Ilmenite Stores	0.10 – 0.24	Filtration	0.10 – 1.00
Millimg	0 – 0.15	Calcination	0
Digestion & reduction	0 – 0.34	Crystallization	0.1 – 10.0
Digester residue store	0.40 – 0.50	Concentration	0 - 0.15
Ti precipitation	0 – 0.15	Neutralization	0 – 0.15

CONCLUSIONS

Nevertheless, in the areas where the instantaneous external dose rates are higher, the worker occupancy is low or very low. Consequently, the effective doses received by the workers due to external radiation, under normal running conditions, are in all cases lower than 1 mSv/year. Only special precautions, from the radiological point of view, should be taken in the crystallisation and filtration areas when the scales are removed during maintenance operations in the plant.